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1 HCC-011

2 **MANUFACTURE AND USE OF A HERBICIDE FORMULATION**

3

4 **RELATED APPLICATIONS**

5 This application claims benefit to US provisional application serial number  
6 60/250,547 filed December 1, 2000 which is incorporated by reference in its entirety for  
7 all useful purposes.

8

9 **Field of Invention**

10 The invention pertains to a method for manufacture and use of a herbicidal  
11 formulation of chlorinated carboxylic acid herbicides.

12

13 **BACKGROUND OF THE INVENTION**

14 Many agricultural formulations contain water-soluble salts of chlorinated  
15 carboxylic acid herbicides. These salts, often alkylamine salts or metal salts, are generally  
16 not as active as their acid equivalents. For example, (2,4-dichlorophenoxy)acetic acid  
17 ("2,4-D") acid is known to be more herbicidally active than the dimethylamine salt of  
18 2,4-D. Also, many of the chlorinated carboxylic acid herbicides are sold to the end users  
19 as esters because these esters are more active than the corresponding amine formulation.  
20 For instance, it is generally known that 2,4-D ester formulations are more effective as  
21 herbicides than 2,4-D amine formulations. The esters, however, are more likely to  
22 volatilize even after deposition onto target areas. After volatilization, these esters can  
23 cause significant damage to off-target plants.

1 Chlorinated carboxylic acid herbicides are usually have traditionally been reacted  
2 into amine or other salts, which are soluble in water, or into esters which are oil soluble.  
3 Both salts and esters must then break down in the environment back into the acid, which  
4 is herbicidal.

5 It would be preferable, then, to apply the herbicides as acids. However, they are  
6 not significantly soluble in water. Previously, solvents used to formulate 2,4-D acid such  
7 as xylene range hydrocarbons, are known to be phytotoxic to plants and may enhance  
8 herbicide volatility and subsequent drift to non-target areas. Albaugh D-638 is one such  
9 product, but it further incorporates the ester form of 2,4-D into the formulation. The  
10 formulation is 24.5 % by weight of 2-butoxyethyl ester of 2,4-dichlorophenoxyacetic acid  
11 (CAS # 1929-73-3), 13.8% by weight 2, 4-D (CAS # 94-75-7) and a solvent that contains  
12 7.7 % by weight naphthalene (CAS # 91-20-3). It is believed that the solvent is Aromatic  
13 150. It is believed that solvent is present in an amount from 55 to 60%. Another  
14 commercial product containing the acid form of 2,4-dichlorophenoxyacetic acid is  
15 WEEDONE® 638 from Rhone Poulenc (now marketed by Nufarm). This formulation  
16 contains 25.2% of the 2-ethylhexyl ester of 2,4-D, 13.8% of the acid form of 2,4-D, 3%  
17 propylene glycol, 1.5% titanium oxide and other undisclosed inerts. This formulation is  
18 believed to be described in one of the following patents: US 5254344, US 5096711, or  
19 US 5206021. The 2,4-D in this formulation is not solubolized, but has been dispersed  
20 through a water phase.

21 Another problem associated with the amine salts of some chlorinated carboxylic  
22 acid herbicides is their inability to mix with fertilizers. 2,4-D amine herbicides cannot be  
23 mixed directly into Uran (urea-ammonia nitrate) fertilizer without some dilution in water.

1 This is a disadvantage for applicators, since this dilution practice increase the total spray  
2 volume they must apply per acre.

3 Surfactants are used in most agricultural formulations to enhance the ease of  
4 application. Since many pesticide formulations use hydrophobic solvents, requiring the  
5 use of surfactants to emulsify the hydrophobic solvent and pesticide into water.

6 Surfactants have also been used both as adjuvants and formulation components to  
7 enhance the effectiveness and spreading ability of applied sprays.

#### 8 9 10 **SUMMARY OF THE INVENTION**

11 We have surprisingly discovered that many chlorinated carboxylic acid herbicides  
12 can be dissolved into surfactants. These surfactant solubolized herbicides are then seen to  
13 have improved spray mix compatibility and improved herbicidal effectiveness. Mixtures  
14 of the 2,4-D acid composition and the dicamba formulation produced under this teaching,  
15 are fully compatible with Uran fertilizers without any dilution.

16 One embodiment of the invention is a herbicide composition comprising at least  
17 one chlorinated carboxylic acid herbicide and at least one surfactant in an effective  
18 amount such that said chlorinated carboxylic acid herbicide is dissolved in the surfactant  
19 and said at least one surfactant is present in a quantity equal to or greater than said at least  
20 one chlorinated carboxylic acid herbicide.

1 Another embodiment of the invention is a herbicide composition comprising at  
2 least one fully solubolized chlorinated carboxylic acid herbicide and at least about 8  
3 weight % of at least one surfactant.

4 The invention also related to a process to produce a herbicidal composition  
5 which comprises blending a fully solubolized acid herbicide with a surfactant to form a  
6 solution provided that said chlorinated carboxylic acid herbicide and surfactant are  
7 present in an amount of about 1 part by weight of chlorinated carboxylic acid herbicide to  
8 at least about 1.5 part by weight of surfactant.

#### 9 10 **DETAILED DESCRIPTION OF THE INVENTION**

11 Again, one embodiment of the invention is a herbicide composition comprising at  
12 least one chlorinated carboxylic acid herbicide and at least one surfactant in an effective  
13 amount such that said chlorinated carboxylic acid herbicide is dissolved in the surfactant  
14 and said at least one surfactant is present in a quantity equal to or greater than said at  
15 least one chlorinated carboxylic acid herbicide.

16 Another embodiment of the invention is a herbicide composition comprising at  
17 least one fully solubolized chlorinated carboxylic acid herbicide and at least about 8  
18 weight % of at least one surfactant.

19 The invention also related to a process to produce a herbicidal composition  
20 which comprises blending a fully solubolized acid herbicide with a surfactant to form a  
21 solution provided that said chlorinated carboxylic acid herbicide and surfactant are  
22 present in an amount of about 1 part by weight of chlorinated carboxylic acid herbicide to  
23 at least about 1.5 part by weight of surfactant.

1 Chlorinated carboxylic acid herbicides include, but are not limited to the acid forms of:

2 Synthetic auxins including, but not limited to:

3 Benzoic acids such as but not limited to chloramben and dicamba,

4 Phenoxy-carboxylic acids such as but not limited to 2,4,5-trichlorophenoxy acetic

5 acid, 2,4-dichlorophenoxy acetic acid, 2,4-dichlorophenoxy butyric acid,

6 clomeprop, dichlorprop, dichlorprop-P, monochlorophenoxy acetic acid,

7 monochlorophenoxy butyric acid, mecoprop, and mecoprop-P.

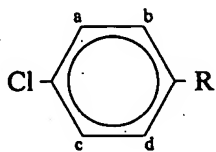
8 Pyridine carboxylic acids such as but not limited to clopyralid, fluroxypyr,

9 picloram and triclopyr.

10 Quinoline carboxylic acids such as but not limited to quinclorac and quinmerac.

11 These herbicides preferably have one of the following 3 general structures

12 Structure 1:

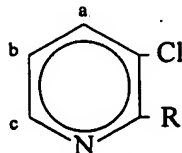


13

14 Wherein R is an alkanoic or carboxylic acid group

15 a,b,c, and d are independently -H, -Cl, -NH<sub>2</sub>, -CH<sub>3</sub>, or -OCH<sub>3</sub>.

16 Structure 2:



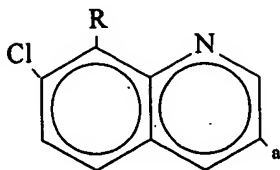
17

18 Wherein R is an alkanoic or carboxylic acid group and

1 a,b and c are independently -H, -Cl, -F, or NH<sub>2</sub>.

2

3 Structure 3:



4

5 Wherein R is an alkanolic or carboxylic acid group and

6 a is -Cl, or -CH<sub>3</sub>

7

8 Useful surfactants or solvents include but are not limited to:

9 Alcohol alkoxylates including but not limited to:

10 Based on branched and linear alcohols

11 Those containing ethylene oxide or propylene oxide

12 Alcohol alkoxylate sulfates,

13 Alkylphenol alkoxylates including but not limited to:

14 Nonylphenol and octylphenols.

15 Those containing ethylene oxide or propylene oxide

16 Alkanolamides,

17 Alkylaryl sulfonates,

18 Amine oxides

19 Amines including but not limited to:

20 Fatty amine alkoxylates such as but not limited to tallowamine alkoxylates,

21 Betaine derivatives,

- 1 Block polymers of ethylene and propylene glycol,
- 2 Carboxylated alcohol or alkylphenol alkoxylates,
- 3 Diols, including but not limited to Butanediols,
- 4 Diphenyl sulfonate derivatives,
- 5 Ethers, including but not limited to
- 6       Butyl celluslove,
- 7       Butyl carbitol,
- 8 Ethoxylated amines,
- 9 Ethoxylated fatty acids,
- 10 Ethoxylated fatty esters and oils,
- 11 Ethylene carbonate,
- 12 Fatty esters,
- 13 Glycerol esters,
- 14 Glycols including but not limited to
- 15       Propylene glycol,
- 16       Ethylene glycol,
- 17       Dipropylene glycol,
- 18       Diethylene glycol,
- 19 Phosphate ester surfactants including but not limited to
- 20       Phosphate esters of alcohol alkoxylates,
- 21       Phosphate esters of alkylphenol alkoxylates,
- 22 Propylene Carbonate,
- 23 Sarcosine derivatives,



- 1   Silicone-based surfactants,
- 2   Sorbitan derivatives including but not limited to:
  - 3       Sorbitan esters,
  - 4       Alkoxylated sorbitan esters,
- 5   Sucrose and glucose derivatives including but not limited to:
  - 6       Alkylpolyglucosides,
- 7   Sulfates and sulfonates of alkoxylated alkylphenols,
- 8   Sulfates of alcohols,
- 9   Tristyrylphenol Alkoxylates,
- 10  Other surfactants are disclosed in McCutcheon's Emulsifiers and Detergents, North
- 11  American Edition, 2000.
- 12  Other surfactants are disclosed in the following patents:
  - US 5741502 Homogeneous, essentially nonaqueous adjuvant compositions with  
buffering capability
  - US 5725630 Dry granular fertilizer blend and a method of fertilizing plants
  - US 5580567 Homogeneous, essentially nonaqueous adjuvant compositions with  
buffering capability
  - US 5393791 Homogeneous, essentially nonaqueous adjuvant compositions with  
buffering capability
  - US 5234919 Water soluble, highly active dimethoate formulations in an alcohol/ester  
solvent system
  - US 5178795 Homogeneous, essentially nonaqueous adjuvant compositions with  
buffering capability

US 5906961 Alkanolamide spreader-sticker surfactant combination

US 5877112 Agricultural formulation

US 6232272 Manufacture and use of herbicide chlorinated phenoxy formulation

The formulations may also contain oil-based components.

The oil or oil substitutes include, but are not limited to:

Alkylated fatty acid esters, include but are not limited to:

Methylated fatty acids, include but not limited to:

Methylated C6-C19 fatty acids,

Methylated Tall oil fatty acids,

Methylated Oleic acid,

Methylated Linoleic acid,

Methylated Linolenic acid,

Methylated Stearic acid,

Methylated Palmitic acid,

And blends thereof;

Ethylated fatty acids, include but are not limited to:

Ethylated C6-C19 fatty acids,

Ethylated Tall oil fatty acids,

Ethylated Oleic acid,

Ethylated Linoleic acid,

Ethylated Linolenic acid,

1 Ethylated Stearic acid,  
2 Ethylated Palmitic acid,  
3 And blends thereof;  
4

5 Butylated fatty acids, include but are not limited to:

6 Butylated C6-C19 fatty acids,  
7 Butylated Tall oil fatty acids,  
8 Butylated Oleic acid,  
9 Butylated Linoleic acid,  
10 Butylated Linolenic acid,  
11 Butylated Stearic acid,  
12 Butylated Palmitic acid,  
13 And blends thereof;  
14

15 Alkylated natural oils, include but are not limited to:

16 Alkylated soybean oil, include but limited to:

17 Methylated soybean oil,  
18 Ethylated soybean oil,  
19 Butylated soybean oil,  
20 And blends thereof;  
21

22 Alkylated canola oil, include but are not limited to:

23 Methylated canola oil,

1 Ethylated canola oil,  
2 Butylated canola oil,  
3 And blends thereof;

4 Alkylated coconut oil, include but are not limited to:

5 Methylated coconut oil,  
6 Ethylated coconut oil,  
7 Butylated coconut oil,  
8 And blends thereof;

9  
10 Alkylated sunflower oil, include but are not limited to:

11 Methylated sunflower oil,  
12 Ethylated sunflower oil,  
13 Butylated sunflower oil,  
14 And blend thereof;

15  
16 Hydrocarbon oils include but are not limited to:

17 Mineral oils, including but are not limited to:

18 Paraffinic mineral oils,  
19 Naphthenic mineral oils,  
20 Aromatic mineral oils,  
21 And blends thereof;

22  
23 Vegetable oils, include but are not limited to:

1 Soybean oil,  
2 Canola oil,  
3 Cottonseed oil,  
4 And blends thereof;

5  
6 Fatty acids, include but are not limited to:

7 C6-C19 fatty acids,  
8 Tall oil fatty acids,  
9 Oleic acid,  
10 Linoleic acid,  
11 Linolenic acid,  
12 Stearic acid,  
13 Palmitic acid,  
14 And blends thereof;

15  
16 Polybutenes

17  
18 Epoxified seed oils include but are not limited to:  
19 Epoxified soybean oil and  
20 Other oils or oil substitutes

21

1 The formulation can contain at least one of the above oils or its equivalent. The oil can  
2 also be a blend of at least two oils. When an oil is used, a surfactant or emulsifier must  
3 also be used if the composition is intended for aqueous based sprays.  
4

5 The composition preferably contains

- 6 (a) from about 1 to about 50% by weight of at least one chlorinated  
7 carboxylic acid herbicide, preferably about 5 to about 30% and most  
8 preferably about 10 to about 20% and  
9 (b) at least about 8% of a surfactant and preferably at least 10% by weight of  
10 a surfactant, more preferably at least 20% by weight of a surfactant, more  
11 preferably at least 30% by weight of a surfactant and even more preferably  
12 from at least 40% by weight of a surfactant and most preferably at least  
13 50% by weight of a surfactant. Again the surfactant can be present in an  
14 amount from about 8 to about 99%, preferably about 50 to about 90%, and  
15 most preferably about 70 to about 80% and  
16 (c) Optionally other components.  
17

18 The composition can further comprises an ester of (2,4-  
19 dichlorophenoxy)acetic acid. The composition according to the invention  
20 preferably contains at most 25% by weight of an ester of (2,4-  
21 dichlorophenoxy)acetic acid, preferably at most about 15% by weight of an ester  
22 of (2,4-dichlorophenoxy)acetic acid, more preferably at most about 10% by  
23 weight of an ester of (2,4-dichlorophenoxy)acetic acid, most preferably at most

1 about 5% by weight of an ester of (2,4-dichlorophenoxy)acetic acid and at most  
2 about 2% by weight of an ester of (2,4-dichlorophenoxy)acetic acid. Of course,  
3 the formulation works with no (2,4-dichlorophenoxy)acetic acid.

4 The herbicide composition can optionally contain an aromatic solvent.

5 The aromatic solvent is present preferably in an amount of at most 50% by  
6 weight and more preferably at most 40% by weight of an aromatic solvent and  
7 even more preferably at most 30% by weight of an aromatic solvent and even  
8 more preferably at most 20% by weight of an aromatic solvent and even more  
9 preferably at most 15% by weight of an aromatic solvent and even more  
10 preferably at most 10% by weight of an aromatic solvent and most preferably at  
11 most 5% by weight of an aromatic solvent.

12 The herbicide composition preferably contains a chlorinated carboxylic  
13 acid herbicide and a surfactant in the ratio of acid herbicide to surfactant from  
14 about 1:6 to about 1:1.

15 The herbicide composition does not need to contain an alkylated fatty  
16 acid, alkylated plant derived oil and/or an alkylated animal derived oil.

17  
18  
19  
20 Examples of these formulations are shown below:

21  
22 Example 1

23 2,4-D Acid Technical 15.0%

1	C <sub>11</sub> Alcohol (3EO) Ethoxylate	85.0%
2		
3		
4		
5	Example 2	
6	Dicamba acid technical	15.0%
7	Nonylphenol (6EO) Ethoxylate	85.0%
8		
9	Example 3	
10	MCPA acid technical	10.0%
11	Pluronic L31	90.0%
12		
13	Example 4	
14	2,4-D acid technical	20.0%
15	Polyoxyethylene (20) sorbitan monolaurate	80.0%
16		
17	Example 5	
18	2,4-D acid technical	30.0%
19	Butyl cellusolve	70.0%
20		
21	Example 6	
22	2,4-D acid	20.0%
23	Methylated soybean oil	30.0%



1	C <sub>11</sub> Alcohol (9EO) Ethoxylate	50.0%
2		
3		
4		
5	Example 7	
6	2,4-D Acid technical	10.0%
7	Dicamba acid technical	10.0%
8	C <sub>11</sub> Alcohol (6EO) Ethoxylate Phosphate ester	80.0%
9		
10	Example 8	
11	2,4-D Iso-octyl ester technical	25.0%
12	Dicamba acid technical	15.0%
13	C <sub>11</sub> Alcohol (3EO) Ethoxylate	60.0%
14		
15	Example 9	
16	2,4-D Acid technical	20.0%
17	Aromatic 150	10.0%
18	C <sub>11</sub> Alcohol (3EO) Ethoxylate	70.0%
19		
20	Example 10	
21	2,4-D P Acid technical	15.0%
22	C <sub>11</sub> Alcohol (3EO) Ethoxylate	85.0%
23		

## 1 Example 11

2	2,4-D B acid technical	15.0%
3	C <sub>11</sub> Alcohol (3EO) Ethoxylate	85.0%

In all of the above examples, the components are blended together and the technical dissolved entirely. The solution formed contains less than 2% of precipitates and preferably 0% precipitates. Surprisingly, these formulations are compatible with Uran 32 fertilizer.

Various additions can be made to the compositions as one may anticipate based on skill in the art. Other pesticides could be formulated using this composition. Fertilizers could be added to these compositions.

All references discussed herein are incorporated by reference in their entirety for all useful purposes.